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(ArBMe$_3$)Li · D complexes (Ar = C$_6$H$_4$CH(X)NMe$_2$-2). Their structure, dynamic molecular processes and the nature of the carbon–lithium bond in the light of multinuclear (^{1}H, ^{13}C, ^{7}Li, ^{11}B) NMR measurements at variable temperature

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Abstract

The lithium "ate" complexes (ArBMe$_3$)Li·D, Ar = C$_6$H$_4$CH(X)NMe$_2$-2, X = H, Me; D = OEt$_2$, THF were synthesized by reaction of Ar$_4$Li$_4$ with BMe$_3$ in coordinating solvent. A monomeric structure with an aromatic C-bridge between lithium and boron, with intramolecular stabilization by CH(X)NMe$_2$ group and intermolecular stabilization by solvent molecules, was detected on the basis of multinuclear NMR of ^{1}H, ^{13}C, ^{7}Li and ^{11}B. Variable temperature NMR measurements (from 173 to 333 K) show intramolecular rearrangements of the investigated complexes. The flexibility of the complexes is examined as a function of acidity of the lithium centre. The NMR of ^{7}Li shows high field shift of the lithium resonances in comparison with the parent organolithium compounds and the results are discussed in terms of the nature of the carbon–lithium bond.

Introduction

Organolithium chemistry has been extensively explored during the last fifteen years [1–3]. A great variety of organolithium compounds RLi (R = alkyl, aryl, vinyl, allyl, cyclopentadienyl) has been synthesized and characterized. In absence of electron donors organolithium compounds form multinuclear aggregates—tetrameric, hexameric and aggregates with higher degree of association. In the presence of electron donors the formation of tri-, di- and monomeric species was detected. In consequence the lithium atom can enter into various types of lithium–carbon bonding e.g. 2 centre – 2 electron, 3c–2e and 4c–2e. On the other hand complexes with the solvated Li$^+$ cation were also reported. The organolithium compounds can react with other organometallic compounds with the formation of bimetallic species. The presence of the other metal centre influences the properties of the organolithium compounds. The investigations of compounds the general formula LiM^{n+}R$_{n+1}$ with M signifying a Main Group metal or transition metal have been developed recently.

Concerning complexes with Main Group elements, a report about the three-dimensional network arrangement of $Li_2Be(CH_3)_4$ with four carbons around a lithium atom was published in 1968 [4]. The compound $Li_2Zn(CH_3)_4$ [5], is isostructural with $Li_2Be(CH_3)_4$. In $(Li \cdot TMEDA)_2Mg(CH_3)_4$ [6] and $[Li \cdot TMEDA \cdot MgPh_3]_2$ [7] the methyl and phenyl groups form bridges between lithium and magnesium. The "ate" organolithium complexes with carbon bridges between lithium and metal (metalloid) have also been reported for Group III elements, e.g.: $LiB(Me)_4$ [8], $LiAl(Et_4)$ [9] and $LiIn(Me_3)_4$ [10]. The anionic aluminates $[Me_2Al(CH_2PMe_2)_2]Li(TMEDA)$ contain a six member $Al(C{-}P)_2Li$ heterocycle [11].

Examples of "ate" complexes with transition metals are as follows. Dimeric complexes $Li_2M_2Ar_4$ (M = Cu, Ag, Au) with various bifunctional and monofunctional aromatic ligands have been isolated and characterized [12,13]. The structure of lithium diorganocuprates $[Li(12\text{-crown-}4)_2][CuMe_2]$, $[Li(12\text{-crown-}4)_2][CuPh_2] \cdot THF$ and $[Li(12\text{-crown-}4)_2][(CuBr)CH(Me_3)_2] \cdot PhMe$ with lithium surrounded exclusively by ether molecules was solved by X-ray diffraction [14]. Recent results concerning lithium "ate" complexes with other transition metals such as Mn and Ni have been published: $Li(THF)_4]_2[Mn_2Ph_6]$ and $[Li(THF)_4][MnMes_3]$ [15], $[Li(TMEDA)]_2[MnMe_4]$, $[Li(TMEDA)]_2[MnEt_4]$ and $[Li(TMEDA)]_2$ $[Mn(CH_2\text{-}CH_2{}^tBu)_4]$ [16], and in [17], the "ate" complexes of methyl lithium with Ni^0. Moreover, complexes with the lanthanides of the type $[Li(dme)_2][(C_2H_5)_2\text{-}Ln(SiMe_3)_2]$, Ln = Sm, Dy, Ho, Er, Tm, Lu have been reported [18].

Review of the above mentioned publications leads to the conclusion that the lithium atom in "ate" complexes, as in organolithium compounds, can be involved either in the ionic bond as stabilized Li^+, or in the multicentre electron-deficient bond, depending on organic substituents and/or electron donor ligands.

Recently we have dealt with the bimetallic $(ArBR_3)Li \cdot OEt_2$ complexes including lithium and boron. We decided to apply the concept of the stabilization of two metallic centres by the bidentate ligand derived from the benzylamine (Fig. 1). This ligand has an enhanced ability to stabilize the complex due to the presence of the intramolecular $CH(X)NMe_2$-donating substituent. The lithium centre is further stabilized by intermolecular donor OEt_2 captured from solvent. The primary results have been published [19]. Recently we have developed the ^{13}C NMR measurements and ^7Li NMR and extended the scope of the investigations and have drawn further conclusions. The following complexes were synthesized: $(Ar^1BMe_3)Li \cdot OEt_2$ (I), $(Ar^2BMe_3)Li \cdot OEt_2$ (II) with the chirality centre in the aryl ligand. $(Ar^1BMe_3)Li \cdot THF$ (III) and $(Ar^2BMe_3)Li \cdot n THF$ (IV). The intramolecular stabilization of the lithium centre with the tertiary amine substituent and intermolecular stabilization with the solvent molecule OEt_2 or THF were established. The structure and intramolecular rearrangements of these complexes in aromatic solvent was established on the basis of variable temperature, multinuclear ^1H, ^{13}C, ^7Li and ^{11}B NMR studies.

Syntheses of $(ArBMe_3)Li \cdot D$ complexes

The $(ArBMe_3)Li \cdot OEt_2$ complexes I and II were synthesized in the course of the reaction of aryl lithium Ar_4Li_4, $Ar = Ar^1$, Ar^2 bifunctional ligands derived from

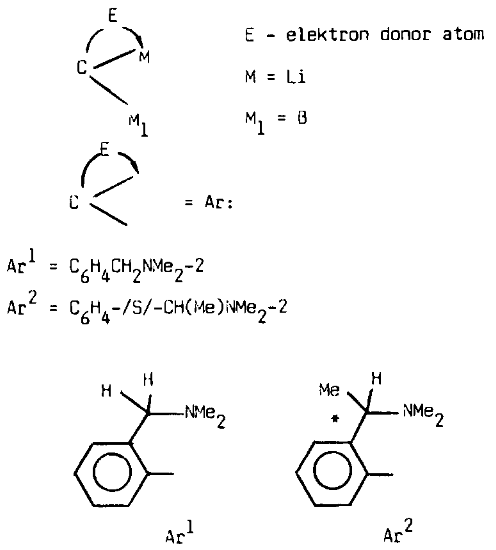

Fig. 1. Dimethyl benzylamine ligands as bidentate donating ligands.

benzylamine: $Ar^1 = C_6H_4CH_2NMe_2$-2 and $Ar^2 = C_6H_4$-(*S*)-CHMeNMe$_2$-2 (Fig. 1) with BMe_3, in ether–hexane solution.

$$Ar_4Li_4 + BMe_3 \xrightarrow{OEt_2/hexane} [ArBMe_3]Li \cdot OEt_2 \qquad (1)$$

$$\text{(I, II)}$$

(I: $Ar = Ar^1$, $D = OEt_2$; II: $Ar = Ar^2$, $D = OEt_2$)

The white solid complexes I and II were precipitated from the concentrated reaction mixture. They were isolated and washed with pentane at low temperature, dried under vacuum and used for the investigations as an amorphous powder. The molecular weight determinations show that the I, II complexes are monomeric in benzene solution.

The $(Ar^1BMe_3)Li$ THF (III) and $(Ar^2BMe_3)Li \cdot n$THF (IV) complexes were synthesized in the donor exchange reaction in boiling THF solution (eq. 2):

$$(ArBMe_3)Li \cdot OEt_2 + THF \xrightarrow{THF} (ArBMe_3)Li \cdot nTHF + OEt_2 \qquad (2)$$

$$\text{(III, IV)}$$

(III: $Ar = Ar^1$, $n = 1$; IV: $Ar = Ar^2$, $n = 3$)

The complexes III and IV were isolated as white solids after concentration of the reaction mixture at low temperature. They were washed with cold pentane and dried under vacuum. They melt slightly at room temperature. Molecular weight determinations show that the complexes III and IV, like complexes I and II, are monomeric in benzene solution.

NMR investigations

The complexes I–IV are stable in aromatic solvents and give slightly opalizing solutions. Multinuclear spectra were run at ^{1}H (250.1 MHz), ^{13}C (62.8 MHz), ^{7}Li

Table 1

^{1}H NMR data of I-IV complexes at various temperatures [a]

Compound	^{1}H NMR (δ ppm)									
	T	H(6)	CH(X)	$OCH_2(OEt_2)$ or OCH_2(THF)	NCH_3	$CH_2(OEt_2)$ or CH_2(THF)	BCH_3	α-CH_3	T_{coal} CH_2	T_{coal} NCH_3
$(Ar^1BMe_3)Li \cdot OEt_2$ [b]	323	7.95dd	3.42	2.83q	1.85	0.58	0.13			
	293	7.50dd	3.41	2.79q	1.80	0.50t	0.13		253	243
	223	7.90dd	4.31	2.33q	1.99br	0.23	0.13			
			($\frac{1}{2}$dd)		1.60br		0.05			
$(Ar^2BMe_3)Li \cdot OEt_2$	323	8.48dd	5.14dd (7.8 Hz)	2.98m	2.11br	0.83	0.55	1.33d (7.8 Hz)		
	293	8.44dd	5.15dd (7.8 Hz)	2.95m	2.08br	0.79	0.60	1.33d (7.8 Hz)		288
	223	8.56dd	5.17dd (7.8 Hz)	2.74m	2.21 1.75	0.74	0.78	1.32d (7.1 Hz)		
$(Ar^1BMe_3)Li \cdot THF$	323	8.34dd	3.75	3.36m	2.11	1.50	0.52			
	293	8.40dd	3.76	3.30	2.10	1.49	0.56		230	223
	223	8.49dd	4.70br ($\frac{1}{2}$dd)	3.09	2.08	1.40	0.72			
$(Ar^2BMe_3)Li \cdot n$THF	243	8.18dd	5.03br	3.56br	1.63	1.79br	0.53			
Ar^1H	RT		3.58		2.08					
Ar^2H	RT		2.06		1.6					

[a] 3–5% solutions in toluene-d_8, referred to residual toluene (CH_n at 2.32 ppm). [b] 20% solution in toluene, referred to internal TMS.

Table 2

^{13}C NMR data of complexes I–IV at various temperatures [a]

Compound	^{13}C NMR (δ ppm)								
	T	C(1)	C(2)–C(6) [b]	$CH_2(OEt_2)$ or $OCH_2(THF)$	CH(X)	NCH_3	BCH_3 $J(^{13}C-^{11}B)$	$CH_3(OEt_2)$ or $CH_2(THF)$	α-CH_3
	r.t.	n.o.		65.5	65.2	44.6	16.2	14.1	
$(Ar^1BMe_3)Li \cdot OEt_2$	233	162.8	140.7	66.3	66.0	45.2	17.2		
(I)		(39.9)	140.1				(40)		
			132.0						
	193	v.w.	128.2	66.5	65.2	46.9	18.0	14.9	
			125.4			43.1	17.9		
$(Ar^2BMe_3)Li \cdot OEt_2$	323	n.o.	145.4	66.0	59.6	39.7	17.0	14.6	6.9
(II)			139.9				(39.6)		
	283	n.o.	127.9	66.0	59.6	n.o.	17.3	14.7	7.0
			126.7				(40.0)		
	253	163.3	125.9	66.1	59.6	44.3	17.4	14.8	
						39.0			
$(Ar^1BMe_3)Li \cdot THF$	323	164 v	140.3	68.6	66.3	45.0	16.8	25.7	
(III)		(39)	139.0				(40.0)		
	293	n.o.	131.7	68.6	66.2	45.1	17.1	25.8	
			127.9				(40.0)		
	223	166.5br	124.6	65.8	68	46br	17.5br	25.9	
$(Ar^2BMe_3)Li \cdot n THF$	293	n.o.	146.0	68.4	60.1	40.5	17.7	26.2	10.9
(IV)			127.0						
	193		126.6	69.1	63.2	45.8	21.3	26.4	10.7
			124.1						
Ar^1H	r.t.				68.28	46.30			
Ar^2H	r.t.				66.19	43.26			

[a] 3–5% solutions in toluene-d_8, referred to toluene (CD_3 carbon at 20.9 ppm). [b] Chemical shifts of the C(2)–C(6) carbons are independent of temperature.

Table 3

^{7}Li and ^{11}B NMR spectral data of complexes I–IV [a]

Compound	^{7}Li [b] NMR spectra		^{11}B [c] NMR spectra
	δ (ppm)	$J(^{13}C-^7Li)$	δ (ppm)
I(Ar^1BMe_3)Li·OEt_2	−0.49	36	−17.2
II(Ar^2BMe_3)Li·OEt_2	−0.72	40	−17.17
III(Ar^1BMe_3)Li·THF	−0.56	34	−17.22
IV(Ar^2BMe_3)Li·nTHF	−0.98	47	−17.41

[a] Solutions in toluene-d_8. [b] Relative to LiCl/D_2O (0.1 M). [c] Relative to BF_3·OEt_2.

(97.2 MHz) and ^{11}B (80.25 MHz) on the Bruker WM-250 MHz. The variable temperature spectra were run in the temperature range from 173 to 335 K. The expected resonance signals (with the right integrations in a case of ^{1}H NMR) were detected for all complexes I–IV. The peak assignments, chemical shift values and coupling constant values, and temperatures of signal coalescence are given in Table 1 (^{1}H), Table 2 (^{13}C) and Table 3 (^{7}Li, ^{11}B). For further details see the Experimental Section.

^{1}H and ^{13}C NMR spectroscopy

The ^{1}H (Table 1) and ^{13}C (Table 2) NMR permitted establishment of the stoichiometry, purity and the structure of the isolated complexes I–IV. The appropriate signals were found in the ^{1}H and ^{13}C NMR spectra, corresponding to the $C_6H_4H(X)NMe_2$-2 ligand (m, 4H, arom; dd, 2H, benzyl CH_2 (or q, 1H, benzyl CHMe)) then a signal (s, 9H) corresponding to 3 Me groups bonded to boron and one to the solvent molecule OEt_2 (d, 4H, CH_2; t, 6H, CH_3) or THF (t, 4H, OCH_2; t, 4H, CH_2) in the following ratios: I (1 : 3 : 1); II (1 : 3 : 1); III (1 : 3 : 1); IV (1 : 3 : 3) (ratio calculated on the whole groups). These patterns correspond to the formula $ArLi \cdot BMe_3 \cdot nD$ ($n = 1$, I–III; $n = 3$, IV). Signals assigned to $ArBMe_2$ which was not separated, though, present to the extent of about 3–4%, were observed in some experiments.

Further analyses of the ^{1}H and ^{13}C NMR spectra show the CH(X)NMe_2 groups are coordinated to lithium via nitrogen atom. The chemical shifts $\delta^1H_{NCH_2}$ deviate from those of the parent amine (Ar^1H or Ar^2H) from 0.02 ppm (III) to 0.48 ppm (II) and those of CH_2 (or CH) benzylic protons are shifted from 0.17 ppm (I) to 2.5 ppm (II). Likewise ^{13}C NMR spectra show the NCH_3 carbons to be shifted from 1.2 ppm (III) to 3.56 ppm (II) and benzylic CH_2 (or CH) carbons from 2.08 ppm (III) to 6.59 ppm (II). These findings are consistent with the fact that the CH(Me)NMe_2 ligand is more basic than the CH_2NMe_2 ligand and that the lithium centre coordinated with OEt_2 is more acidic than that coordinated with THF. The spectra are temperature dependent and at decreased temperatures the presence of the diastereotopic Me groups bonded to nitrogen (abbreviated further as NMe_2 groups) was detected for complexes I–II. With increasing temperature they coalesce to one singlet (I: $T_c = 243$ K, $\Delta G^{\ddagger} = 59.37$ kJ/mol *; II: $T_c = 288$ K, $\Delta G^{\ddagger} = 64.78$ kJ/mol; III: $T_c < 223$ K). Besides, the CH_2 protons from the benzylic group in I and III, at

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* The $\Delta G^{\ddagger}$ value was calculated from the equation $\Delta G^{\ddagger} = 19.14 \cdot T_c \cdot (9.97 + \log T_c)$ (J/mol).

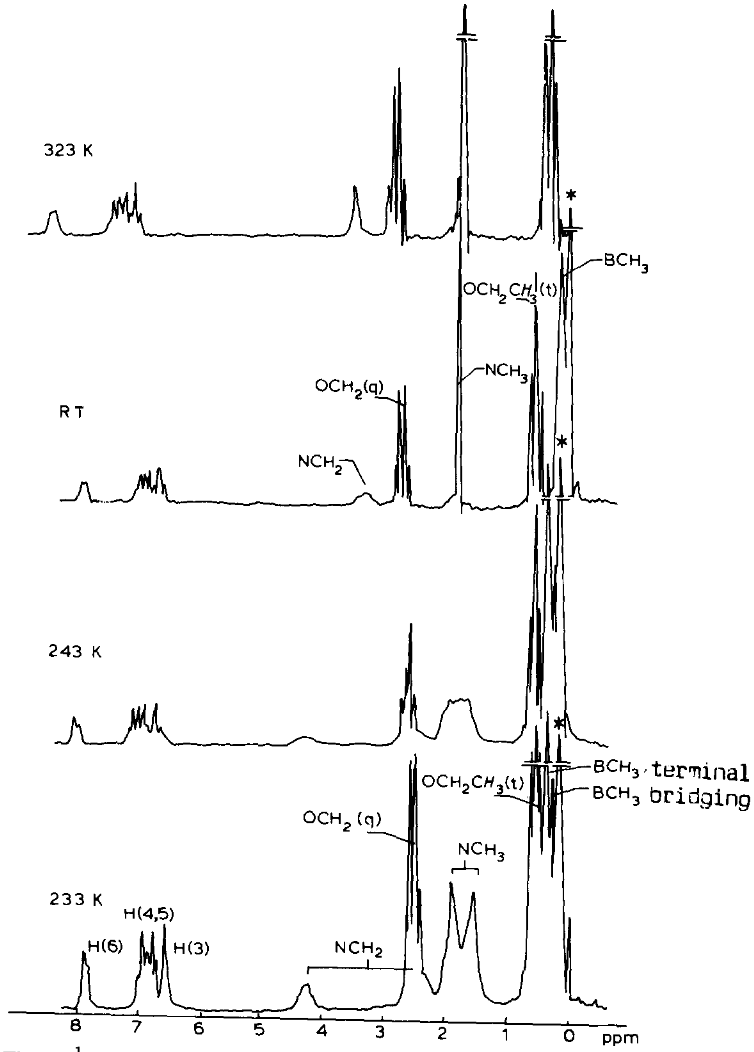

Fig. 2. ^{1}H NMR spectra of (Ar^{1}BMe$_3$)Li·OEt$_2$ in toluene-d_8, with TMS (peak with asterisk) as an internal standard at various temperatures.

low temperature, were detected as the AB patterns, which also coalesce with increasing temperature (Fig. 2). These phenomena show that (ArBMe$_3$)Li · D complexes are flexible in solution; their dynamic behaviour will be discussed later. The energy barriers depend on the basicity of the nitrogen atom and on the acidity of the lithium centre with coordinated donor molecules, either OEt$_2$ or THF.

The OEt$_2$ or THF donor molecules are coordinated to the lithium as shown by the chemical shift values of CH$_2$, δ^1H or δ^{13}C (Tables 1 and 2) compared to the values of noncoordinated molecules, e.g.: 3.16 (δ^1H: OCH$_2$(OEt$_2$)); 68.28 ppm (δ^{13}C: OCH$_2$(OEt$_2$)) and 3.16 [δ^1H: OCH$_2$(THF)); 68.4 ppm (δ^{13}C: OCH$_2$(THF)). The number of coordinated molecules, as mentioned before, is 1 for I–III complexes and 3 for complex IV.

The next stage in the examination of the products I–IV is the analysis of the *ortho*-chemical shift of the H(6) protons in the aromatic ring. These H(6) protons resonate in the range 7.9–8.5 ppm, which shows the presence of the polarized C(1)–metal bond. The C(1) carbons are detected at low field in the range 160–164 ppm. Although these carbons are of very low detectability due to a long relaxation time and quadrupolar effects of lithium and boron nuclei, variable temperature NMR permit detection of C(1) signals for I–III and the coupling constant $J(^{13}C-^{11}B) = 40$ Hz for I and III. The appearance of this coupling constant indicates that the new bond C(1)–B was formed in the course of reaction 1.

^{7}*Li NMR spectroscopy*

The ^{7}Li spectra show the presence of a single signal for each compound I–IV. For the complexes formed from the $Ar^2{}_4Li_4$ substrate the ^{7}Li NMR provides proof that the aryllithium substrate resonating at 3.75 ppm has been converted in the new compound. The results of the measurements are collected in Table 3. The values of the chemical shifts fall into the range -0.49 ppm to -0.98 ppm. The differences of the chemical shifts values of the investigated complexes I–IV are rather small, but in comparison with the total scale of ^{7}Li NMR covering approximately 6 ppm they are quite informative, as will be shown further. Careful referencing is required in these measurements.

^{11}*B NMR spectroscopy*

In ^{11}B NMR spectra, as in ^{7}Li NMR single signals for each I–IV complex were detected (Table 3). The signals corresponding to three coordinative boron atom in BMe_3 at 86 ppm [20] were not observed indicating that BMe_3 was converted to the new "ate" complexes resonating at -17 ppm. These values are typical for the four coordinative boron atom. The differences between chemical shifts values are very small, from 0.03 to 0.24 ppm, which is in agreement with the close similarity of the boron environments in the investigated complexes I–IV.

Discussion

The analysis of the multinuclear NMR results establishes that in complexes I–III the $1/4Ar_4Li_4$, BMe_3 and OEt_2 (or THF) molecules are bonded in the ratio 1 : 1 : 1. Consequently the stoichiometry of these complexes is $ArLi \cdot BMe_3 \cdot OEt_2$ (or THF). Exceptionally, a higher number of THF molecules is incorporated in complex IV. ^{1}H and/or ^{13}C NMR spectra, observed at low temperature indicate diastereotopic amine methyl groups and the AB pattern for CH_2 benzylic protons in complex I and III and this indicates: first, the nitrogen from CH_2NMe_2 group is coordinated to the acidic (in Lewis sense) centre and second, a chirality centre is formed in these complexes. In accordance with NMR results this chirality centre is formed at the aromatic C(1) carbon bonded to lithium and boron. This conclusion is supported by ^{11}B NMR spectroscopy showing complexation of BMe_3 molecules with the increase of the coordination number from 3 to 4 and ^{13}C NMR indicating generation of the coupling constant $J(^{13}C-^{11}B) = 39.9$ Hz on C(1) carbon signals. The coordination of the donor molecule to lithium as previously mentioned was also established on the basis of NMR measurements. The presence of terminal and bridging methyl groups bonded to boron (abbreviated as BMe), in the ratio 2 : 1 was observed in ^{1}H

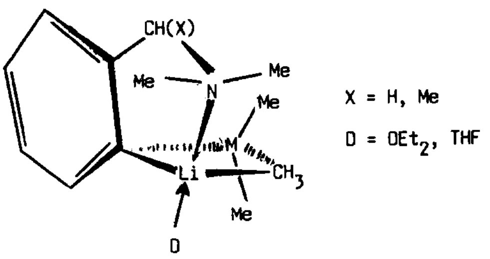

Fig. 3. The structure of complexes I–III.

NMR at 233 K in the spectra of complex I. Unfortunately in the spectra of complex II and III the signals of the B–Me groups and the triplet of the methyl group from the OEt_2 molecule superimpose and broaden at low temperature which makes interpretation difficult. In ^{13}C NMR the B–Me carbons are also observed at low temperature as broad signals due to relaxation and quadrupolar effects. However we assume that in complexes II and III there is the same arrangement of the B–Me groups as in complex I. On the basis of the complete NMR measurements, we deduce the structure of complexes I–III (Fig. 3). The BMe_3 molecule is complexed to the C(1) aromatic carbon. Together with lithium the atom, the boron atom forms a 3c–2e bond with carbon. One of the methyl groups, bonded to boron, bridges between the same lithium and boron atoms. The molecule is stabilized by the intramolecular coordination of nitrogen from $CH(X)NMe_2$ group, which is in a favourable position for such coordination. The lithium atom coordinates additionally one donor solvent molecule (ether or THF) on its fourth unoccupied coordination site. While the acidity of lithium is decreased as in complex IV, by coordination of stronger bases ($CH(Me)NMe_2$ and THF), the CH_3 bridge is not formed.

The variable temperature NMR patterns of the CH_2NMe_2 group in our complexes indicated the presence of the chirality centre on C(1). Therefore we decided to use the C_6H_4-(*S*)-$CHMeNMe_2$-2 ligand with its chirality centre at the benzylic carbon for the synthesis of the complex II with two chirality centers: on benzylic and C(1) carbons respectively. Two diastereoisomers were expected with *SR* and *RR* configurations, distinguishable in NMR spectra. However in NMR spectra only one diastereoisomer was detected indicating that the reaction 1 is stereoselective. The examination of steric interactions in the *SR* and *RR* diastereoisomers (Fig. 4) shows that if the $CH(Me)NMe_2$ group is coordinated to lithium, the methyl group

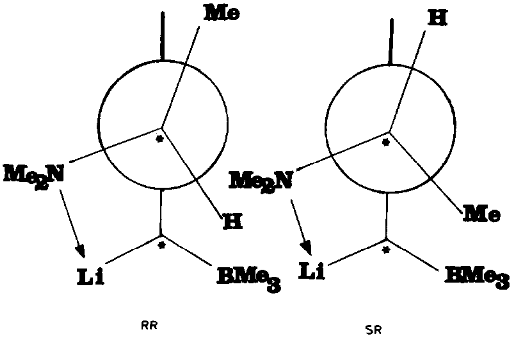

Fig. 4. The Newman projection of *S*(*R*) and *R*(*R*) $(Ar^2BMe_3)Li \cdot OEt_2$ diastereomers.

bonded to methine carbon approaches closer the methyl groups bonded to boron in the *SR* isomer than in the *RR* one. The *RR* isomer is less crowded and presumably this is the favoured one.

Since the spectra of complexes I–III are temperature dependent, dynamic rearrangement of the complexes can be observed. The changes of H(6) and C(1), benzylic CH_2, NCH_3, BMe_3 (complex I) patterns in both ^1H and ^{13}C NMR were observed. Two diastereotopic NMe_2 group signals, and the AB pattern of benzylic CH_2 proton signals coalesce with increasing temperature. These phenomena show that the molecules of the complexes are flexible in solution. The nitrogen atom of the $CH_2N(CH_3)_2$ group is coordinated to lithium at low temperature. It dissociates at higher temperature, and inversion of configuration on nitrogen atom can occur resulting in averaging of the Me group signals. The averaging of an AB pattern, observed at low temperature in I and III complexes, is due to the inversion of configuration at C(1). In other words, at low temperatures with slow intermolecular rearrangement rate (relative to NMR time scale) the sharp signals of two NMe_2 groups and protons of CH_2 are observed. They broaden and coalesce when the rate of exchange is higher with rising temperature, while in the fast exchange range of temperature they again become sharp, but NMe_2 groups (I–III) and CH_2 protons (I, III) are indistinguishable. The molecules are nonrigid and the inversion of configuration proceeds on nitrogen and at C(1) carbon. These rearrangements are accompanied by the exchange of BMe groups between terminal and bridging positions as shown by ^1H NMR. The variable NMR spectra of complex II are different in the range of methylene protons since the invariable quartet of CH protons is observed, however the above mechanistic considerations are relevant also to this molecule. The same phenomena have been previously established for other organolithium "ate" complexes, comprising bifunctional $C_6H_4CH(X)NMe_2$-2 (X = H, Me) ligand [12].

In complex IV, unlike in complexes I–III, three molecules of donor (THF) are coordinated to lithium. The chemical shifts in the spectra of complex IV depend on temperature, however only one methyl group from noncoordinated CH_2NMe_2 is observed at low temperature. The spectra exhibit changes that are not typical for I–III complexes, which means that the same explanation of the dynamic behaviour of the molecule is not reliable in this case. The lithium resonance was observed at highest field, demonstrating electron rich lithium environment. We assume that in this case the acidity of the lithium atom coordinated to $CHMeNMe_2$ is too low to form the Li-CH_3 bond and the C(1)LiCB core is not formed. Then, as a result of competition, the lithium cation is stabilized with three THF molecules. Unfortunately the obtained NMR spectra do not provide more details of this structure.

It is interesting to ask what the nature of the lithium–carbon bond is. The electron deficient bond of the aromatic carbon with two lithium nuclei consists of hybridized *p*-carbon and *p*-lithium orbitals. For two different metals with different electro-negativity the bond is not symmetrical any more and in a borderline case it is more like the σ bond with a lithium cation complexed to an aromatic ring via its *s* orbital (Fig. 5). In our case the 3c–2e Li–C(1)–B bond is formed in I–III complexes. This bond can be polarized to an extent that depends on acidity of coordinated lithium and basicity of $M^{n+}R_{n+1}$ unit. For complex IV with less acidic lithium stabilized with three THF molecules we postulated cationic interaction with π-electrons of an aromatic ring.

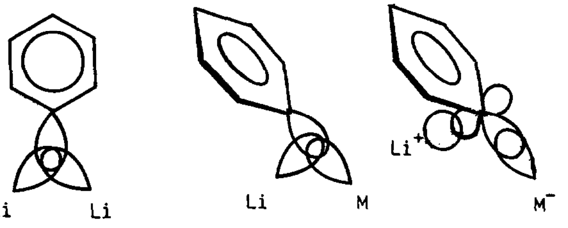

Fig. 5. The polarized 3c–2e Li(C1)M bond with an aromatic carbon.

There are a few data in the literature [2g] which lead to the conclusion that the value of ^{7}Li NMR chemical shifts can correlate with the degree of lithium–carbon bond polarization. If we consider the ^{7}Li chemical shifts values (Fig. 6) it should be noted that the signal of the most acidic lithium with the coordinated weak donors, (nitrogen from CH_2NMe_2 and the OEt_2 molecule) was detected at −0.49 ppm. Then the signal of less acidic lithium with the coordinated nitrogen of CH_2NMe_2 group and THF (stronger base than OEt_2) was observed at −0.56 ppm. The lithium atom with coordinated $CHMeNMe_2$, which is a much stronger base than CH_2NMe_2, and with coordinated OEt_2 was observed at −0.72 ppm. Finally the lithium atom with coordinated $CHMeNMe_2$ and 3 THF molecules, expected to be least acidic and not able to form a LiC_2B ring was recorded at -0.98 ppm. In this sequence the chemical shifts at higher fields indicate a higher degree of lithium–carbon bond polarization. However, this remark applies only to the same type of compounds. One has to be careful with the general interpretation of ^{7}Li chemical shifts and further research is still required.

We considered the correlation between polarity of the lithium carbon bond and the dynamic properties of the complexes I–III. As already mentioned these complexes are flexible in solution, some of them even at low temperature. The diagram (Fig. 7) shows the dynamics of complexes I–III as a function of temperature. The complexes I–III are depicted in their different rearranged forms: at the base is a static molecule, in the middle is a molecule with dissociated N–Li bond, then at the top there are molecules undergoing inversion of configuration at C(1). Complex III

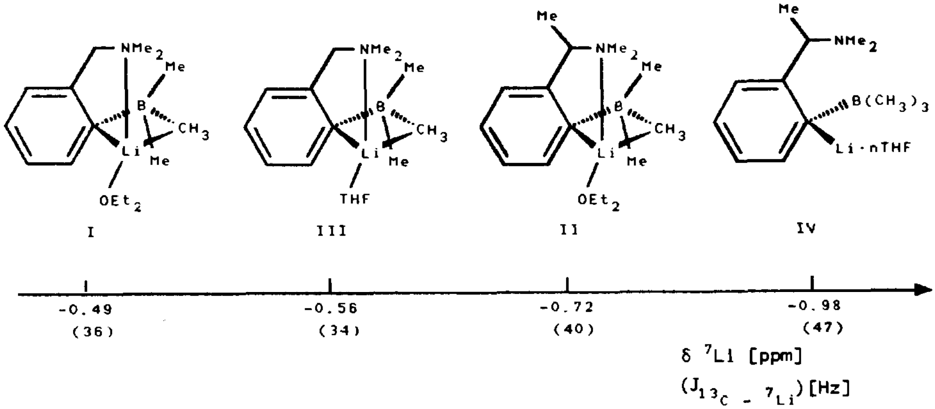

Fig. 6. ^{7}Li chemical shifts of complexes I–IV.

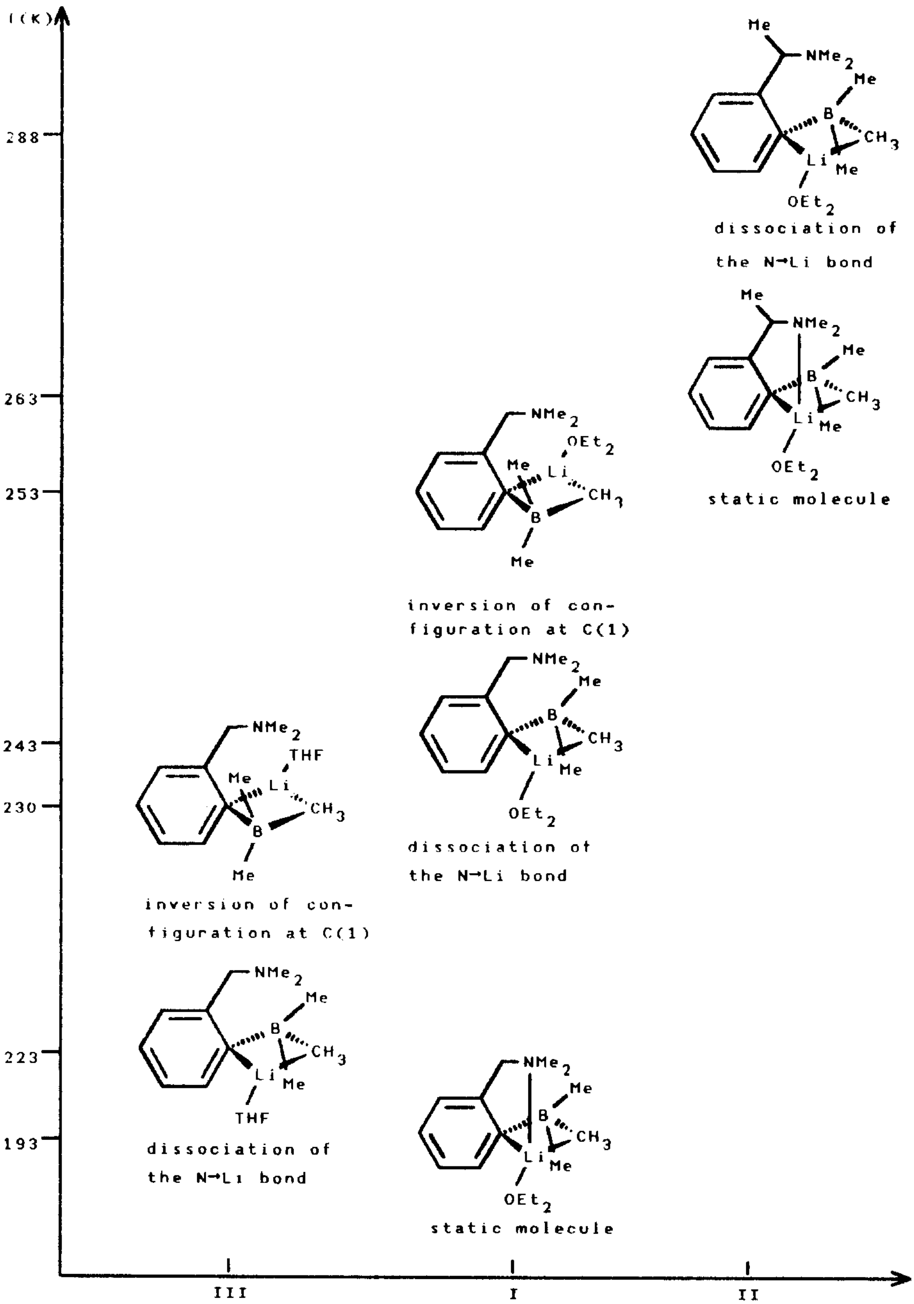

Fig. 7. The intramolecular rearrangements of complexes I–III as a function of temperature.

with THF donor, less acidic with respect to the lithium–carbon bond, is still flexible below 233 K. Complex I is static below 243 K and nonrigid above 253 K, and complex II is static at 263 K and flexible at 293 K. However there is no accurate correlation between ^{7}Li chemical shifts, e.g. acidity of the lithium centre and dynamics of the investigated complexes. The only conclusion which can be drawn is that the flexibility of the compounds depends on numerous factors such as temperature, polarity of the lithium carbon bond and the relative basicity of the inter- and intramolecular donating ligands.

Experimental

All experiments were performed under dried and deoxidized N_2 using standard oven dried Schlenk tubes. The solvents and solutions were transferred by means of syringes or double ended needles. Solvents were kept over molecular sieves, and then distilled from K/benzophenone ketyl.

The standard ^1H NMR spectra were recorded with a JEOL JNM-100H, ^{13}C NMR spectra with a Varian CST 20 (100 MHz) spectrometers. The VT experiments were run on the Bruker WM-250 spectrometer. The samples in 5 mm tubes in 20% concentration were used for the JEOL JNM-100H (^1H) measurements. Samples in 10 mm tubes at 20% concentration were used for Varian 100 MHz (^{13}C) and at 2–5% concentration for VT-FT Bruker WM 250 experiments. No essential differences were observed in the spectra recorded for these concentrations. The NMR tubes were filled under nitrogen using a vacuum-nitrogen line, closed with plastic caps and measured immediately after preparation. No signs of decomposition of the compounds were observed after VT experiments.

The ^1H NMR spectra were referred to the residual methyl protons at 2.32 ppm, ^{13}C NMR spectra to the toluene-d_a methyl carbon at 20.8 ppm, ^7Li NMR spectra to $LiCl/D_2O$ (0.1 M) with the correction for the difference between the lock frequencies of D_2O and toluene-d_8, ^{11}B NMR spectra to the $BF_3 \cdot OEt_2$ complexes.

Preparation of BMe_3 (based on [21])

A solution of MeI (85.14 g, 0.6 mol) in 100 ml of butyl ether was added dropwise to magnesium wires (14.1 g, 0.6 mol) in 50 ml of butyl ether. The reaction was carried out overnight. To the reaction mixture approximately 5 ml of $BF_3 \cdot OEt_2$ complex was added slowly. Generated BMe_3 was directly used for the preparation of complexes I and II. All precautions for the work with air flammable, explosive and highly volatile BMe_3 were taken.

Preparation of $(Ar^1Li)_4$ and $(Ar^2Li)_4$

These lithium aryl compounds were prepared according to Ref. 22.

Preparation of $(Ar^1BMe_3)Li \cdot OEt_2$ (I) and $(Ar_2BMe_3)Li \cdot OEt_2$ (II)

$(Ar^1Li)_4$ (1.36 g, 9.6 mmol) was suspended in 50 ml of ethyl ether in a 100 ml Schlenk tube and $(Ar^2Li)_4$ (0.68 g, 4.4 ml) of was dissolved in 30 ml of ethyl ether in another 100 ml Schlenk tube. The Schlenk tubes were connected with Tygon tubes in a row and gaseous BMe_3 was passed through, till the excess of BMe_3 was observed in the bubbler placed behind the reaction flasks. The solutions were concentrated to one fourth of the starting volume, cooled, and the precipitated white solids were separated and washed with cold pentane. 2 g of I was obtained (yield 77%) and 0.78 g of II (yield 62%).

Preparation of $(Ar^1BMe_3)Li \cdot THF$ *(III)*

$(Ar^1BMe_3)Li \cdot OEt_2$ (I) (0.5 g, 1.85 mmol) was dissolved in 10 ml of THF and kept under reflux for 2 h. The reaction mixture was concentrated to one fourth of the starting volume and cooled with stirring in dry ice/acetone bath. The white precipitate was formed, decanted and washed with cold pentane. After drying under vacuum at room temperature 0.28 g (yield 56.3%) of III was obtained as sticky solid.

Preparation of $(Ar_2BMe_3)Li \cdot 3THF$ *(IV)*

IV was obtained from $(Ar_2BMe_3)Li \cdot OEt_2$ (II) (0.5 g, 1.76 mmol) according to the procedure described for III. Yield: 0.31 g (61.6%).

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